Cleavage of a phosphorus carbon triple bond in the reaction of 2,2-dimethylpropylidynephosphine with $[Os_3(CO)_{10}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Me)]$

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The reaction of 2,2-dimethylpropylidynephosphine with the cluster $[Os_3(CO)_{10}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Me)]$ 1 results in P–C bond cleavage and an insertion of the precoordinated but-2-yne ligand into the phosphorus carbon triple bond of the incoming phosphaalkyne with formation of a novel bridging C_3P-moiety in the structurally characterised complex $[Os_3(CO)_8(\mu_2\text{-}PCBu^t)\{\mu_3\text{-}PC(Me)C(Me)C(Bu^t)\}]$ 2, together with a second $\mu_2\text{-}\eta^2,\eta^2$-ligated phosphaalkyne.

The coordination chemistry of phosphaalkynes RC≡P is of current interest and its similarity to the coordination behaviour of alkynes has been summarised in several recent reviews.[1] In particular, the use of phosphaalkynes as alkyne-like building blocks in the formation of phosphorus containing unsaturated ring systems is of considerable synthetic use.[1,2] Despite several examples of controlled alkyne–alkyne coupling reactions at polynuclear carbonyl clusters,[3] in all our previous attempts to achieve an oligomerisation of phosphaalkynes in the coordination sphere of triruthenium and triosmium carbonyl clusters, we isolated products exclusively resulting from a carbonylation of the incoming $Bu^tC{\equiv}P$ to afford the phosphinidene ligand $\mu_3\text{-}PC(CO)Bu^t$, *e.g.* in the complexes $[M_3(CO)_9\{\mu_3\text{-}PC(CO)Bu^t\}_2]$ (M = Ru, Os) and their derivatives.[4] The thermodynamic sink represented by the formation of these complexes is apparently efficient enough to prevent any phosphaalkyne oligomerisation. In an attempt to avoid this dominating pathway and also to facilitate alkyne-like reactions, we decided to modify the reaction system by introducing a precoordinated alkyne unit, a strategy that also proved to be successful in case of an Ir_4 carbonyl cluster system.[5] Here, we wish to present the results of the reaction between 2,2-dimethylpropylidynephosphine and the alkyne cluster $[Os_3(CO)_{10}(\mu_3\text{-}\eta^1,\eta^2,\eta^1\text{-}C_2Me_2)]$ **1**.

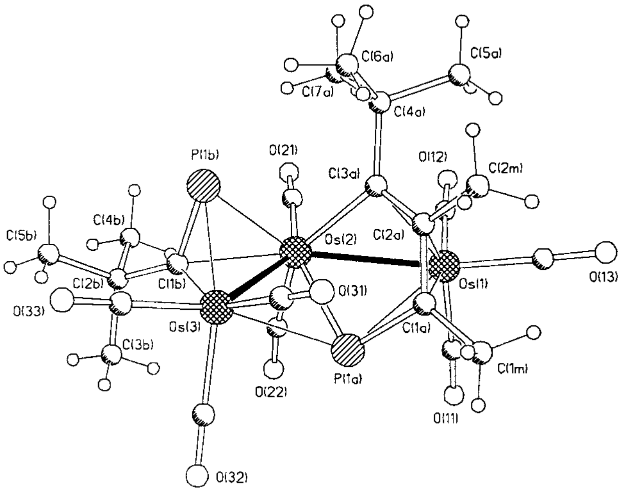


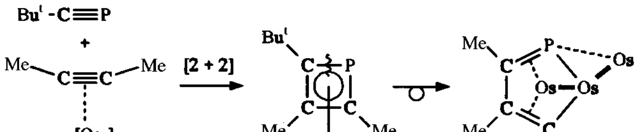
Fig. 1 Molecular structure of $[Os_3(CO)_8(\mu_2\text{-}PCBu^t)\{\mu_3\text{-}PC(Me)C(Me)C(Bu^t)\}]$ **2** with atom numbering scheme. The carbonyl carbon atoms bear the same numbers as the respective oxygen atoms. Selected bond lengths (Å) and angles (°): Os(1)–Os(2) 2.8130(8), Os(2)–Os(3) 2.8217(7), Os(1)–P(1A) 2.701(3), Os(2)–P(1A) 2.368(3), Os(3)–P(1A) 2.666(3), Os(1)–C(1A) 2.227(11), Os(1)–C(2A) 2.271(12), Os(1)–C(3A) 2.283(12), Os(2)–C(3A) 2.209(12), P(1A)–C(1A) 1.790(12), C(1A)–C(2A) 1.42(2), C(2A)–C(3A) 1.43(2), C(1A)–C(1M) 1.501(14), C(2A)–C(2M) 1.53(2), C(3A)–C(4A) 1.56(2), Os(2)–P(1B) 2.423(3), Os(2)–C(1B) 2.257(12), Os(3)–P(1B) 2.424(3), Os(3)–C(1B) 2.111(11), P(1B)–C(1B) 1.731(12), C(1B)–C(2B) 1.53(2), mean Os–C(CO) 1.929(25), mean C(CO)–O(CO) 1.141(18); Os(1)–Os(2)–Os(3) 117.09(2), P(1A)–Os(2)–Os(1) 62.14(8), P(1A)–Os(2)–Os(3) 61.08(8), C(3A)–Os(2)–P(1A) 83.8(3), C(3A)–Os(2)–Os(1) 52.4(3), C(1A)–P(1A)–Os(1) 55.1(4), C(1A)–P(1A)–Os(2) 99.8(4), C(1A)–P(1A)–Os(3) 108.8(4), P(1A)–C(1A)–C(2A) 118.4(8), P(1A)–C(1A)–C(1M) 116.8(8), C(2A)–C(1A)–C(1M) 123.6(11), C(1A)–C(2A)–C(3A) 120.8(11), C(1A)–C(2A)–C(2M) 114.0(10), C(3A)–C(2A)–C(2M) 125.2(10), C(2A)–C(3A)–C(4A) 119.6(11), C(1B)–Os(2)–Os(3) 47.5(3), C(1B)–Os(2)–P(1B) 43.2(3), P(1B)–Os(2)–Os(3) 54.41(7), C(2B)–C(1B)–P(1B) 132.3(9).

The reaction of cluster **1** with 1 equiv. of $Bu^tC{\equiv}P$ in refluxing CH_2Cl_2 resulted in the formation of cluster $[Os_3(CO)_8(\mu_2\text{-}PCBu^t)\{\mu_3\text{-}PC(Me)C(Me)C(Bu^t)\}]$ **2**, which was formulated on the basis of spectroscopic data† and the results of a single crystal structure analysis.‡

In addition to an edge-bridging $\mu_2\text{-}\eta^2:\eta^2$-coordinated phosphaalkyne moiety, this unusual complex bears an additional ligand formed by the coupling of the initial $\mu_3\text{-}\eta^1:\eta^2:\eta^1$-butyne ligand with a second phosphaalkyne molecule. The insertion of this ligand into the bond between Os(1) and Os(3) opens the metal triangle forming a bent three metal chain, with the phosphorus atom P(1a) bridging all three osmium atoms.

Together with the central osmium atom Os(2), this ligand forms a 1-osma-2-phosphacyclopentadiene ring which binds to the terminal osmium atom Os(1) in the η^5-coordination mode. This central five membered ring is essentially planar with the atoms deviating from the best plane by ±0.0579 Å.

It is of special significance, that it is not the ring carbon atom C(1a) vicinal to the phosphorus atom P(1a) which bears the Bu^t substituent of the former phosphaalkyne moiety but carbon atom C(3a). Therefore, the phosphorus carbon triple bond of this precursor is completely cleaved during the course of the reaction leading to the formation of **2**, and a plausible explanation for this finding is represented in Scheme 1. The insertion of the osmium atom Os(2) into a phosphorus carbon bond of an intermediate phosphacyclobutadiene ligand, formed in a [2 + 2]-cycloaddition of the but-2-yne and the phosphaalkyne, leads to the formation of the observed 1-osma-2-phospha-



Scheme 1 Hypothetical mechanism for the formation of the $\{\mu_3\text{-}PC(Me)C(Me)C(Bu^t)\}$-subunit in **2**

cyclopentadiene ring. There are relatively few examples of co-cyclodimerization reactions of alkynes and phosphaalkynes at transition metal centres resulting in phosphacyclobutadiene metal complexes that are comparable to the proposed intermediate.[6] Although no information regarding the detailed mechanism outlined in Scheme 1 is available, it is interesting to note that, since only one regioisomer is isolated, insertion into the proposed phosphacyclobutadiene intermediate occurs exclusively at the bond between the phosphorus and the carbon atom bearing the Bu^t substituent.

The fact that the basic open Os$_3$-triangle in the framework of **2** requires a total of 50 valence electrons with a contribution of four valence electrons from the second μ_2-η^2,η^2-coordinated phosphaalkyne ligand indicates that the central ligand formed by the coupling of butyne and Bu^{t}C≡P acts as a six electron donor. Therefore, it can be concluded that the lone pair centred on P(1a) does not contribute to the cluster framework. The coordination around phosphorus atom P(1a) can be described as a distorted square based pyramid with the three osmium atoms forming the base together with the carbon atom C(1a), while the lone pair of P(1a) points into the direction of the apex.

While the distances between Os(2) and either P(1a) or C(3a) are 2.368(3) and 2.209(12) Å, respectively, lying within the range of normal Os–P and Os–C single bonds,[7] the distances between P(1a) and either Os(1) or Os(3) are *ca.* 30 pm longer than the average [2.701(3) and 2.666(3) Å, respectively]. This indicates a very unusual bonding situation because steric reasons for the observed bond lengthening can be excluded at least in the case of the interaction between Os(3) and P(1a).

The second phosphaalkyne ligand in **2** bridges Os(2) and Os(3) in the μ_2-η^2,η^2-coordination mode with the participation of both P–C π-MOs. The P–C distance of the side on coordinated phosphaalkyne is 1.731(12) Å, which is too short for the expected single bond but easily fits the range of typical P–C double bonds.[7] The Bu^t substituent on the methylidyne carbon atom C(1b) bends away from the osmium atoms as a result of a rehybridisation caused by the coordination, thereby reducing the angle P(1b)–C(1b)–C(2b) from 180° in the free phosphaalkyne to 132.3(9)°. Similar features have been reported for the only other structurally characterized example of a side on-coordinated phosphaalkyne ligand, [Mo$_2$Cp$_2$(CO)$_4$(μ_2-$\eta^2:\eta^2$-PCBu^t)],[8] where the P–C distance is 1.719(3) Å and the P–C–C angle 127.9(3)°.

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Notes and References

† *Synthesis of* **2**: A mixture of 37.9 mg (0.042 mmol) [Os$_3$(CO)$_{10}$(μ_3-$\eta^1:\eta^2:\eta^1$-C$_2$Me$_2$)] **1**[9] and 4.2 mg (0.042 mmol) 2,2-dimethyl-propylidyne-phosphine[10] in 50 ml of dry CH$_2$Cl$_2$ was heated under reflux for 24 h under an inert atmosphere. After filtration and concentration *in vacuo,* **2** was separated from unreacted starting material by thin layer chromatography [silica gel, CH$_2$Cl$_2$–hexane (3 : 7)] as the only major product (6%). Yellow crystals suitable for X-ray crystallography were grown by vapor diffusion of hexane into a CH$_2$Cl$_2$ solution. ^{1}H NMR [(CD$_3$)$_2$CO], δ 1.43 (s, 9H, Bu$^{t(b)}$), 1.60 (s, 9H, Bu$^{t(a)}$), 2.41 (s, 3H, Me^{2m}), 2.68 (s, 3H, Me^{1m}); ^{31}P NMR (CDCl$_3$), δ −118.0 (P^{1b}), 229.7 (P^{1a}); IR (CH$_2$Cl$_2$), ν_{CO} 2080s, 2050vs, 2023s, 2014s, 1993m, 1970m cm^{-1}; FABMS (MeCN/3-noba), *m/z* 1054 − 28*n*, $0 \leqslant n \leqslant 8$, [M − *n* CO]$^+$.

‡ *Crystal data* for **2**·0.5 CH$_2$Cl$_2$: C$_{22}$H$_{24}$O$_8$Os$_3$P$_2$ + 0.5 CH$_2$Cl$_2$, M_w = 1091.41, monoclinic, space group *C*2/*c*, a = 31.052(4), b = 11.315(2), c = 17.258(2) Å, β = 108.394(10)°, U = 5753.9(13) Å^3, Z = 8, D_c = 2.520 Mg m^{-3}, T = 150 ± 2 K, F(000) = 3992, μ(Mo-Kα) = 13.463 mm^{-1}, yellow needle, 0.23 × 0.08 × 0.06 mm. Intensities of 5861 reflections were collected between $2.73 \leqslant \theta \leqslant 25.06°$ on a STOE Stadi 4 diffractometer using Mo-Kα radiation (graphite monochromator, ω scan mode). Absorption corrections were applied using ψ-scan data: T_{min} = 0.136, T_{max} = 0.224. The structure was solved by direct methods[11] and refined by full-matrix least-squares on F^2. A molecule of CH$_2$Cl$_2$ lies disordered over four positions about the crystallographic two-fold axes (two unique orienations plus their symmetry equivalents; Z for the CH$_2$Cl$_2$ is thus 4, compared to 8 for the Os cluster and hence this is the hemidichloromethane solvate). The occupancy ratio of the unique molecules refined to 0.29 : 0.21(1), with two common isotropic displacement parameters being respectively refined for the C and Cl atoms. The positional parameters were refined subject to explicit geometry restraints [C–Cl 1.80(2), Cl–Cl 2.93(2) Å]. All other non-H atoms were refined freely with anisotropic displacement parameters.[12] Final R values: R_1 = 0.0418 and wR_2 = 0.0805 [based on F^2 and 5082 data with $I > 2\sigma(I)$ and 345 parameters]. The final Fourier difference map showed no residual density outside of −1.378 and 1.303 e Å^{-3}. CCDC 182/1010.

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